International Food Research Journal 23(5): 2203-2206 (2016)
Journal homepage: *http://www.ifrj.upm.edu.my*

Determination of Na and K in Brazilian solid dietary sweeteners by flame photometry

[1*]Oliveira, A.P., [1]Martins, D.L., [2]Martins, M.L. and [2]Villa, R. D.

[1]Federal Institute of Education, Science and Technology of Mato Grosso (IFMT), Campus Cuiabá - Bela Vista, 78050-560, Cuiabá, Mato Grosso, Brazil
[2]Department of Chemistry, Institute of Exact and Earth Sciences (ICET), Federal University of Mato Grosso (UFMT), Campus Cuiabá, 78000-000, Cuiabá, Mato Grosso, Brazil

Article history

Received: 15 October 2015
Received in revised form: 5 January 2016
Accepted: 6 January 2016

Keywords

FAES
Solid dietary Sweeteners
Metals

Abstract

The aim of this work was to develop a method for the determination of Na and K in Brazilian solid dietary sweeteners by flame photometry. Five types of sweeteners were employed, and the samples were prepared by dissolution in deionized water. The analytical curves showed linear correlation coefficients (r) higher than 0.99. The detection limit (LD) and quantification (LQ) were 0.13 and 0.40 mg L^{-1}, and 0.18 and 0.55 mg L^{-1}, for Na and K, respectively. The LQ values were low enough for the quantification of Na and K at concentrations down to 0.1 mg g^{-1}. Recoveries ranged from 79 to 119%, with RSD lower than 8%. The Na and K concentrations measured in the commercial products depended on the types of artificial sweeteners used in the formulations. The proposed method offers a straightforward, rapid, and inexpensive alternative for the determination of Na and K in solid dietary sweeteners.

Introduction

The consumption of diet food has grown in Brazil and worldwide. Data from the Brazilian Association of Diet Food (ABIAD) indicate that 35% of Brazilian households consume a diet product, especially sweeteners, whose consumption has grown by about 600% over the last eight years (ABIAD, 2014). These diet products have been the object of much polemic, in large part due to the carcinogenic properties attributed to compounds such as aspartame, sodium cyclamate, and sodium saccharin, amongst others (Thomas *et al.*, 1986; Henin 2001; Weihrauch *et al*., 2004). At the same time, there are few studies in the literature concerning the inorganic composition of these foods, particularly with respect to the concentrations of metal species (Maihara *et al.*, 2001; Porfírio *et al.*, 2006; Souza *et al*., 2006; Souza *et al*., 2007).

The commonest artificial sweeteners consumed in Brazil are sodium (Na) and potassium (K) salts such as sodium saccharin, sodium cyclamate, and acesulfame potassium (Pachione, 2003). These metals influence the osmotic pressure of blood and intercellular fluids, and assist in transmitting electrochemical impulses in nerve and muscle fibers. Excessive concentrations of the metals in the human body are associated with increased blood pressure, heart and kidney diseases, and hyperkalemia (Engstrom *et al*., 1997; Molina *et al*., 2003; Riella, 2003). The average daily per capita intake of sodium in Brazil is 3.8 g, which is about 40% higher than the amount recommended by the World Health Organization (2.3 g) (WHO, 2012). Recently, the Brazilian Ministry of Health and the Brazilian Association of Processed Food Producers signed a commitment to gradually reduce the level of sodium in foods by approximately 68% (ANVISA, 2013). With the increasing need to control Na and K concentrations in foods, there is a growing requirement for suitable methods for the determination of these metals.

The cost-effective quality control of food products demands the development of analytical methods that are not only inexpensive, but also simple, precise, and accurate. At present, the determination of metals in dietary sweeteners is usually performed by inductively coupled plasma optical emission spectrometry (ICP-OES) or neutron activation analysis (NAA) (Soliman *et al.*, 1999; Maihara *et al.*, 2001; Porfírio *et al*., 2006; Souza *et al*., 2006; Souza *et al*., 2007). These techniques generally provide low limits of detection and quantification, but have high operational and maintenance costs.

Flame atomic emission spectrometry (FAES) is the most simple and inexpensive spectroanalytical technique for the determination Na and K in biological fluids, soils, fuels, and other matrices (Lajunen and Peramaki, 2004), and can also be a useful tool for the measurement of metals in foods. The aim of

*Corresponding author.
Email: *adriana.oliveira@blv.ifmt.edu.br*

this study was therefore to develop a method for the determination of Na and K in different Brazilian solid dietary sweeteners using FAES.

Materials and Methods

Instrumentation

An Analyser® Model 910 flame photometer was used for the determination of Na and K. The measurements were carried out according to the manufacturer's recommendations for maximum sensitivity, with petroleum gas and compressed air as the combustion gases. The aspiration rate of the working standard solutions or samples was adjusted to 2.00 ± 0.2 mL min^{-1}. An analytical balance (±0.0001 g accuracy, Model 210A, Bel Marck, Monza, Italy) was used for weighing the samples. Micropipettes (Boeco, Germany) with adjustable volumes of 5–50 µL, 50–200 µL, and 100–1000 µL were used to dispense the solutions.

Reagents, solutions, and samples

High purity deionized water (resistivity 18.2 MΩ cm, Milli-Q system, Millipore, Bedford, MA, USA) was used for the preparation of the standard solutions and samples. The standard solutions were prepared by sequential dilution of 1000 mg L^{-1} aqueous Na and K stock solutions (Carlo Erba, Italy). All flasks and glassware were washed with tap water, immersed in 7.0% (v/v) HNO_3 solution for at least 24 h, and rinsed thoroughly with deionized water.

Five Brazilian solid dietary sweetener samples, composed of different natural and artificial compounds, were obtained locally in the city of Cuiabá, Mato Grosso State, Brazil. The samples were labeled A1-A5, and the different sweeteners were identified using the labels E1-E6, corresponding to sodium cyclamate, sodium saccharin, sucralose, acesulfame potassium, aspartame, and stevioside, respectively. The samples contained E1+E2 (A1), E3+E4 (A2), E5 (A3), E1+E2+E4+E5 (A4), and E6 (A5).

Instrumental parameters

The linearity was evaluated by means of the linear correlation coefficients (r) for analytical curves constructed with Na and K aqueous standards in the concentration range 0.0-50 mg L^{-1} (Ribani *et al.*, 2004). The LD and LQ were determined according to the method described by Currie (1999). All measurements were made in triplicate (n = 3) and included an analytical blank.

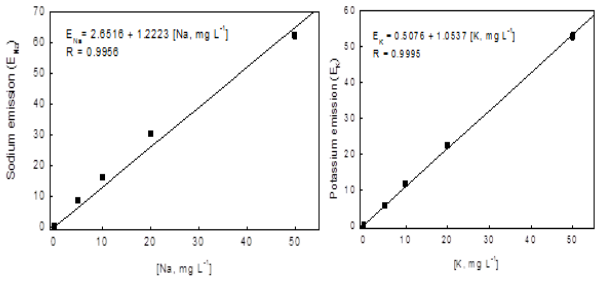

Figure 1. Analytical curves for Na and K in aqueous solutions in the concentration range 0.0–50.0 mg L^{-1}

Sample preparation

With the exception of sample A1, which contained a high concentration of sodium, sample preparation consisted of adding 0.2 g portions of the substances to 50 mL volumetric flasks, which were completed with deionized water. In the case of sample A1, a mass of 0.1 g was used in order to avoid unnecessary further dilution.

Addition and recovery tests

The accuracy of the proposed method was assessed using addition and recovery tests at three concentration levels: 1.25, 2.50, and 5.00 mg g^{-1} of Na and K for sample A1, and 0.625, 1.25, and 2.50 mg g^{-1} of Na and K for the other samples. These tests were conducted by adding different volumes of 1000 mg L^{-1} aqueous spectroscopic Na and K standards to the sweetener samples. After the addition, the samples remained at rest for 24 h to permit sample/metal interaction. The addition and recovery tests were performed in triplicate, followed by an analytical blank.

Results and Discussion

The analytical curves showed r values higher than 0.99 for Na and K, indicating a good linear correlation between the analytical signal and the analyte concentration (Figure 1). The limits of detection and quantification were 0.13 and 0.40 mg L^{-1}, and 0.18 and 0.55 mg L^{-1}, for Na and K, respectively. The LQ values were sufficiently low to permit the quantification of Na and K in the samples at concentrations as low as 0.1 mg g^{-1}.

The relative standard deviations (RSD%) of ten consecutive measurements of the lowest concentration Na and K standards were 5%, indicating good instrumental precision. The analytical blank gave an instrumental signal of zero, indicating an absence of interferences.

In the addition and recovery tests, considering all concentration levels, the recoveries varied in the

Table 1. Percentage recoveries of Na and K (n = 3) from spiked solid dietary sweetener samples (mean ± RSD%)

Sample	Recovery (%) ± RSD (%)							
	Na				K			
	Fortification level (mg g^{-1})							
	0.625	1.25	2.50	5.00	0.625	1.25	2.50	5.00
A1	*	113 ± 4.0	91 ± 6.0	108 ± 2.9	---	92 ± 2.2	114 ± 0.0	106 ± 2.7
A2	79 ± 8.0	100 ± 3.5	108 ± 1.0	*	86 ± 2.0	97 ± 1.9	104 ± 0.0	*
A3	86 ± 2.8	95 ± 0.0	117 ± 0.8	*	103 ± 2.2	113 ± 0.0	109 ± 0.5	*
A4	91 ± 4.0	92 ± 5.0	118 ± 4.0	*	94 ± 5.0	107 ± 6.0	107 ± 2.8	*
A5	106 ± 2.0	119 ± 2.0	117 ± 0.5	*	92 ± 2.2	102 ± 0.0	104 ± 1.1	*

*Not evaluated.

ranges 79-119% (Na) and 86-114% (K). The RSD% values were <8.0% (Na) and <6.0% (K) (Table 1). For analyte concentrations in the region of 0.1% (w/w), recoveries in the range 95-105%, with R.S.D of about 6%, are considered acceptable (Taveniers *et al*., 2004; Wood, 1999). It should be noted that a wider range of percentage recovery and R.S.D values may be acceptable, depending on the purpose of the analysis, the complexity of the matrix, and the analytical method employed (AOAC, 1998).

The developed method was used for determination of the analytes in five major brand sweeteners consumed in Brazil. Two different calibration methods were used in these analyses: external standards (ES) and standard additions (SA) (Table 2). There were no significant differences between the concentrations obtained using the two calibration methods (p = 0.05), which demonstrates the accuracy of the method and indicates that the matrix had no effect on the analytical signal.

The Na and K concentrations were related to the types of artificial sweeteners used. For example, sample A1 was composed of sodium cyclamate and sodium saccharin, while sample A2 consisted of acesulfame potassium and sucralose. In Brazil, the main sources of Na and K in solid dietary sweeteners are in the form of artificial compounds such as cyclamate, saccharin, and acesulfame.

In one of the sweeteners evaluated, the sodium concentration exceeded 8.0 mg g^{-1}, although the concentration was not indicated on the label. An individual can easily consume about 6.0 g of solid dietary sweetener daily, equivalent to 48 mg of Na in the case of sample A1. According to the Brazilian Society of Cardiology (SBC), the recommended daily intake of NaCl is 6.0 g, equivalent to around 2.3 g of sodium. Hence, in the case of sample A1, the intake of sodium in the form of solid dietary sweetener would be about 2.0% of the recommended daily intake (Molina *et al*., 2003). It should be noted that for hypertensive individuals, the recommended daily intake of Na must be less than 2.3 g/day, so that the contribution from dietary sweeteners could become significant.

Table 2. Concentrations of Na and K (mg g^{-1}) in the solid dietary sweeteners, determined using the ES and SA calibration methods (mean ± RSD%)

Sample	Analyte concentration (mg g^{-1})			
	ES		SA	
	Na	K	Na	K
A1	8.10 ± 5.0	0.23 ± 0.00	8.15 ± 6.0	0.22 ± 4.0
A2	≤ LQ	1.40 ± 0.00	≤ LQ	1.37 ± 2.0
A3	≤ LQ	≤ LQ	≤ LQ	≤ LQ
A4	4.41 ± 10	0.60 ± 0.00	4.40 ± 6.0	0.62 ± 2.0
A5	0.38 ± 1.0	0.17 ± 0.00	0.40 ± 0.00	0.15 ± 3.0

Conclusions

The findings indicate that flame photometry offers an attractive alternative analytical technique for the determination of Na and K in solid dietary sweeteners. The method developed is simple, rapid, and has low operational and maintenance costs. Sample preparation requires only a single step, and the results of addition and recovery tests, as well as the figures of merit, indicated that the precision and accuracy of the technique are sufficient for quantification of the analytes in real samples, which could be especially useful for the purposes of quality control. The analysis of commercial products indicated that the intake of sodium in the form of solid dietary sweeteners is small, relative to the daily maximum intake recommended by the World Health Organization. Nonetheless, individuals with special dietary requirements should remain vigilant in the case of artificial sweeteners based on sodium salts.

Acknowledgment

The authors thank the Laboratório de Análises de Contaminantes Inorgânicos (LACI) of the Federal University of Mato Grosso (UFMT) by the availability of the equipment and reagents for the execution of this work.

References

Agência Nacional de Vigilância Sanitária (ANVISA) (November, 2013). Anvisa vai monitorar

alimentos que devem reduzir presença de sal. Retrieved on January 04,2015 from ANVISA Website *http://portal.anvisa.gov.br/wps/content/anvisa+portal/anvisa/sala+de+imprensa/menu+-+noticias+anos/2013+noticias/anvisa+vai+monitorar+alimentos+quem+devem+reduzir+presenca+de+sal*.

Associação Brasileira da Indústria de Alimentos para Fins Especiais e Congêneres (ABIAD) (July,2013). O Mercado Diet & Light. Retrieved on January 03, 2015 from ABIAD Website *http://www.abiad.org.br/pdf/mercado_diet_light_novo*.

AOAC. 1998. Association of Official Analytical Chemists. Official method of analysis of AOAC international, 16th edn. Arlington: AOAC.

Currie, L.A. 1999. Detection and quantification limits: origins and historical overview. Analytica Chimica Acta 391: 127-134.

Engstrom, R., Tobelmann, C. and Albertson, A.M. 1997. Sodium intake trends and food choices. The American Journal of Clinical Nutrition 65: 704S-707S.

Henin, N. 2001. Intake of sweeteners, physiological and nutritional aspects. International Sugar Journal 103: 346-351.

Lajunen, L.H.J. and Peramaki P. 2004. Spectrochemical analysis by atomic absorption and emission. Cambridge: Royal Society of Chemistry.

Maihara, V.A, Fávaro, D.T, Silva, V.N, Gonzaga, I.B, Cunha, I.L. and Cozzolino, S.M.F. 2001. Analysis of mineral constituents in duplicate portion diets of two university student groups by instrumental neutron activation. Journal of Radioanalytical and Nuclear Chemistry 249(1): 21 – 24.

Molina, M.C.B, Cunha, R.S, Herkenhoff, L.F and Mill, J.G. 2003. Hipertensão arterial e consumo de sal em população urbana. Revista de Saúde Pública 37(6): 743-750.

Pachione R. 2003. Indústria do diet engorda as vendas. Revista Química e Derivados 419: 38-50.

Porfirio, D.M. and Oliveira, E. 2006. Determinação de alguns elementos em adoçantes artificiais por ICP OES. Revista Analytica 21: 60-70.

Ribani, M., Bottoli, C.B.G., Collins, C.H., Jardim, I.C.S.F. and Mello, L.F.C. 2004. Validação em métodos cromatográficos e eletroforéticos. Quimica Nova 27: 771-780.

Riella, M.C. 2003. Princípios de nefrologia e distúrbios hidroeletrolíticos. Rio de Janeiro: Guanabara Koogan.

Soliman, K. and Zikovsky, L. 1999. Determination of Br, Ca, Cl, Co, Cu, I, K, Mg, Mn, Na, Rb, S, Ti and V in Cereals, Oils, Sweeteners and Vegetables Sold in Canada by Neutron Activation Analysis. Journal of Food Composition and Analysis 12(2): 85-89.

Sousa, R,A., Baccan, N. and Cadore, S. 2006. Analysis of liquid stevioside and cyclamate-saccharin dietetic sweeteners by inductively coupled plasma optical emission spectrometry without sample treatment. Journal Brazilian Chemical Society 17(7): 1393-1399.

Sousa, R.A, Ribeiro, A.S, Antunes, M.V, Curtius, A.J, Baccan, N. and Cadore, S. 2007. Determination of trace elements in liquid aspartame sweeteners by ICP OES and ICP-MS following acid digestion. Microchimica Acta. 159: 241-246.

Taveniers, I., De Loose, M. and Bockstaele, E.V. 2004. Trends in quality in the analytical laboratory. II. Analytical method validation and quality assurance. Trends in Analytical Chemistry 23(8): 535-552.

Thomas, G., Garnier, R. and Fournier, E. 1986. Mutagenicity of urine after ingestion of saccharin in man. Annales de Medeccin Interne 137: 576-578.

Weihrauch, M.R. and Diehl, V. 2004. Artificial sweeteners--do they bear a carcinogenic risk?. Annals of Oncology 15: 1460-1465.

Wood R. 1999. How to validate analytical methods. Trends in Analytical Chemistry 18: 624–632.

World Health Organization. 2012. Guideline: Sodium intake for adults and children. Geneva: World Health Organization (WHO).